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THE DEVELOPMENT OF SILICA HOLLOW
MICROSPHERES FOR USE AS A HIGH
TEMPERATURE DIELECTRIC

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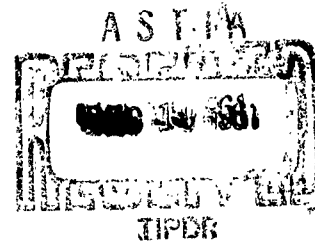R. S. LOTHROP

EMERSON AND CUMING, INC.

JULY 1961

AERONAUTICAL SYSTEMS DIVISION

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THE DEVELOPMENT OF SILICA HOLLOW
MICROSPHERES FOR USE AS A HIGH
TEMPERATURE DIELECTRIC

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Emerson and Cuming, Inc.

July 1961

Aeronautical Systems Division
Air Force Systems Command
United States Air Force
Wright-Patterson Air Force Base, Ohio

FOREWORD

This report was prepared by Emerson & Cuming, Inc. under USAF Contract No. AF33(616)-7263. This contract was initiated under Project No. 7371, "Applied Research in Electrical, Electronic, and Magnetic Materials," Task No. 73710, "Applied Research on Dielectric Materials." The work was administered under the direction of the Physics Laboratory, Materials Central (now designated Directorate of Materials and Processes), Deputy for Technology, Wright Air Development Division (now designated Aeronautical Systems Division), with Mr. W. G. D. Frederick acting as project engineer.

This report covers work conducted from June 1960 through December 1960.

Emerson & Cuming, Inc. manufactures glass microbubbles under license from Standard Oil Company (Ohio). Sohio has continued development work. Their work consisted of process improvement, modification of composition and finally the design, constructions, and test operation of a pilot plant high temperature (1450°C) unit for production of microbubble of vitreous silica. The work was done by Mr. Harvey Alford under the direction of Dr. E. C. Hughes and Dr. F. Veatch, all of Sohio's Chemical and Physical Research Division. The information they obtained was transmitted to us and used extensively in our work. This information is designated in the text of this report.

It should be emphasized that the work done by Sohio is completely independent of the contract period reported on herein. Sohio received no financial support from contract funds.

The help of Professor P. L. T. Brian of Massachusetts Institute of Technology in designing the high temperature furnace is gratefully acknowledged.

Some of the dielectric measurements at low frequencies were made by Mr. W. B. Westphal of the Laboratory for Insulation Research of Massachusetts Institute of Technology.

ABSTRACT

Silica microbubble material has been produced by two routes. The direct process melts particles of silica and expands them into bubbles at 1700°C. Yields of only 5%, primarily because of loss as slag, excessive fuel requirements, and the relatively high true density, 0.8 g/cc, of the product, made the other process the more desirable one. Acid-leaching of the 16% sodium glass bubbles which are made commercially at 950°C, followed by dehydration at 1140°C gave a product having a true density of 0.26 g/cc. It had a slightly lower dielectric constant, 1.11 to 1.2, and equivalent loss tangent values, less than 0.001, at all frequencies and temperatures below 400°C.

Both materials were bonded into sheet structures using cold set cement type bonds without serious degradation of the dielectric properties. These structures withstand moderate loads at 1100°C and do not collapse at 1300°C. Densities range from 0.6 to 1.2 g/cc.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

J. I. WITTEBORT
Chief, Thermophysics Branch
Physics Laboratory
Materials Central

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I   INTRODUCTION

The purpose of this work is production of materials having low, <2.0 dielectric constants and low, <0.008 dissipation factors which are physically and dielectrically useful at temperatures greater than 200°C.   Minimum change in dielectric properties with temperature is also desirable.

Pure silica was the only material we found which approached the desired combination of thermal and dielectric properties.   In order to reduce the dielectric constant of the product, a silica structure having a reduced density was sought.

The work reported on here is a continuation of work done under Contract AF33(616)-5840, Project 7340, and reported in WADD-TR 60-899 Part I.

That report covered laboratory scale process development and a pilot plant campaign for the production of pure silica microbubbles, development work on production of low sodium content microbubbles from sodium silicate glass bubbles by an acid leaching process, and exploratory work on methods for bonding these bubbles into structural shapes.

II DISCUSSION

A. Low Sodium Content Microbubbles by Acid Leaching

Several months' experience with acid-leached bubbles produced by the standard pilot plant procedure [1], 0.15 lb. of bubbles per lb. of 8% H_2SO_4 solution agitated for 15 minutes, washed free of acid and dried, showed that the product would not consistently withstand 900°C without sintering.

Previous work indicated that the primary function of the acid leaching was removal of sodium and that the critical sodium content for 1090°C stability was between 5 and 8%. The thermal stability test as made by pyrometric cones was not satisfactory since it was extremely dependent on density of the cone structure and rate of heating, probably because sodium oxide is somewhat volatile even at 700°C. Porosity, a large exposed surface and slow heating all combine to volatilize alkali and raise the fusion point. Thus material that withstood 1370°C indefinitely in a pyrometric cone sintered and partially fused at 1100°C when molded in a 3" x 3" x 2" block and heated at the same rate. Consequently, it was decided that actual sodium content would have to be the controlled value.

Sodium analyses without special equipment are too time consuming for routine control so a procedure for "extractable alkalinity" as a measure of sodium content was developed. Microbubble product containing 4, 6, and 8% Na by analyses as well as some 30 production lots of acid leached material were used in developing the procedure and setting up a standard for low sodium content microbubbles which would not sinter at 1090°C.

Extractable Alkalinity of Low Sodium Content Microbubbles: Ten grams of microbubbles in 150 mil distilled water is boiled under reflux for 16 hours. A convenient aliquot of the clear solution is titrated to pH 4.0 with N/10 HCl. Milliequivalents of acid required is reported as grams of Na extracted per gram of microbubbles.

All materials having less than 0.009 g extractable Na per gram of microbubbles showed less than 5% linear sintering shrinkage after heating to 1050°C in four hours and holding at that temperature for two hours. This value of extractable alkalinity was therefore established as a control maximum for low sodium microbubbles.

Typical values of various materials are shown in Table 1.

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(1) TR 60-899 Part I - p. 11

Table 1

Alkali Content and Properties of Various Microbubble Products

Material	Ext. Na%(a)	Na%	Temp. Limit°C(b)	Density, g/cc Bulk	Density, g/cc True
1. Na borosilicate bubble "Eccospheres R"(ER)	12.0	16.0	480	0.24	0.41
2. Leached ER, 15 min. in 16% H_2SO_4	6.7	8.4	650	---	---
3. Leached ER, 60 min. in 10% H_2SO_4	4.0	6.3	840	---	---
4. Leached ER, 240 min. in 15% H_2SO_4 "Eccospheres SI"	0.9	3.7	1100	0.18	0.26
5. Leached ER, 480 min. in 16% H_2SO_4	0.4	---	>1200	---	---
6. Leached ER, 120 days in 90% H_2SO_4	<0.05	---	>1200	0.14	0.25
7. Leached ER, 120 days in 35% HCl	<0.05	---		0.15	0.24
8. Leached ER, 3 days in 16% HCl at 100°C	<0.05	---		0.15	0.24
9. Direct Process Silica		<0.2		0.56	0.77

(a) By procedure described above.

(b) 3 cm cubes, density 0.6-1.0 g/cc, heated at 250°C/hr. to temperature and held two hours, with less than 5% linear shrinkage.

Hygroscopicity of some of these materials was obtained by exposing 10 g samples (with 50 cm^2 exposed surface) in a static atmosphere that was approximately saturated with water vapor at room temperature. The percentage increase in weight is an indication of the hygroscopicity of the material .

Table 2

Water Vapor Absorption of Microbubble Products at 90-95% R-H, 24-30°C

Material	3 Wt. gain, %	8 Wt. Gain, %	Physical Condition
Eccospheres R, 16% Na	14	22	caked
ER, 60 min. in 10% H$_2$SO$_4$, 6% Na	12	17	caked
ER, 240 min. in 12% H$_2$SO$_4$, 4% Na	9	9	free flowing
ER, 120 days in 35% HCl	10	11	free flowing
Direct Process Silica 0.2% Na	2	3	free flowing

With the exception of the hydrochloric acid leached material, hygroscopicity decreased as alkali content decreased.

Several proprietary materials formulated to deposit a hydrophobic layer on hydrophilic surfaces were applied to these microbubbles following the manufacturer's recommendations. Armour Chemical Company's Armoflo, a long hydrocarbon-chain quaternary ammonium compound, as well as duPont's Volan and Quilon, both organic chromium complex materials, were tested for effectiveness by exposure of treated microbubbles at 75 and 90% relative humidity. Armoflo slightly decreased the caking of Eccospheres R but did not decrease hygroscopicity of any of the microbubble materials. Volan caused some decrease in moisture pick up at 75% relative humidity but none at 90% R. H. These materials appear to be without any real value in decreasing water vapor absorption.

B.   Production of Silica Microbubbles by the Direct Process

Two campaigns using the pilot plant described in Part I of TR 60-899 were made. Experience gained in the previous campaign permitted smoother operation at higher operating temperatures. All feed stock had 1% glycerine as the blowing agent since this had given the best results in the previous campaign.

During the first week of continuous operation 41 hours of feeding were obtained. Ninety percent of this was at temperatures above 1550°C. Six shut downs were required for clean-out of slag accumulated in the furnace. Initially, these shut downs required 13 hours, including the time required to cool down to a temperature permitting the use of steel bars in the furnace, removal of slag, and reheating to operating temperature. A slag removal bar with forced circulation of cooling water all the way to the working tip made slag removal at a much higher temperature practical and reduced the down time for slag clean-out to 4.5 hours. Two size ranges of feed stock were used. These were nominally -100+200 mesh and -200 mesh. A total of 29500 g was fed at rates ranging from 4.0 g/min. to 20 g/min. Upward combustion gas velocity at operating temperature varied from 4.5 to 9.2 ft./sec. depending on fuel rate, since approximately stoichiometric fuel-air ratio was maintained at all times.

An operating temperature of 1725°C was readily obtained using 1.8 cfm propane and the stoichiometric amount of air. Oxygen enrichment was not used because the desired temperature was attained without it. The improved fuel practice of this campaign over the previous one in which 2.4 cfm propane was required to obtain a 1600°C operating temperature was achieved by frequent flue-gas analyses and the adjustment of the fuel-air ratio based on them.

The primary independent variables were feed stock particle size, operating temperature and feeding rate. Dependent variables (usually determined on 500 g batches of feed) were yield, volume percent of product floating on water and rate of slag formation.

The previous campaign had indicated that in the 1640-1700°C operating range -200 m feed stock gave the best results. With this as a basis, tests on -200 m feed stock were made in the following temperature ranges: 1560-1600, 1600-1650, 1650-1690, 1690-1720. Sixty-four volume percent floaters, the highest value, was obtained while operating between 1620 and 1640°C. Even at this temperature a substantial portion of the product estimated at 20 to 30%, was solid glass balls 10 to 15 microns in diameter. This material was certainly overheated. It appears that particle size of the feed is critical. Temperature and sojourn time adequate for bubble formation from the larger particles causes shrinkage and collapse of bubbles formed from the smaller particles of feed stock.

Above 1650°C accumulation of slag was rapid when feeding minus 200 mesh material. Amount of product and proportion of bubbles in it decreased rapidly whenever there was any quantity of slag accumulation in the lower part of the furnace. It seems likely that slag accumulation increased turbulence in the hot zone and tended to throw more material against the walls where it stuck.

Coarser, nominally -100+200 mesh, feed was used at temperatures between 1675 and 1750°C. Slag accumulation was so rapid that little product was obtained. The product was a mixture of 100 to 200 micron pieces which had a few to numerous bubbles in each piece and small, usually less than 20 microns, almost spherical pieces of solid glass. It appears that temperature and sojourn were inadequate for bubble formation from the larger pieces of feed, but at the same time excessive for the smaller pieces, so that formed bubbles fused and collapsed. These small pieces of molten solid material probably caused the rapid accumulation of slag. The screened feed stock had 25% -200 mesh material in it. It seems likely that this undersize increases the rate of slag accumulation.

Thirty-three percent of the feed was recovered as product in the cyclones and spray chamber. Slag on the furnace walls amounted to 57% of the feed and 10% of the material fed was unaccounted for. Fifteen percent of the product had a true density of less than one gram per cubic centimeter.

The previous campaign had indicated that loss of product by slag formation was probably made more severe by the wide particle size distribution range of the feed stock. To get closer sizing of the finer screen fractions, they were hydroseparated with a rising water current having a vertical component of 10 cm per minute at a dilution that insured free settling conditions. This gave a product containing 4% minus 30 micron material, so that its nominal particle size range was 80 to 40 microns.

It was planned to feed this material at several operating temperatures between 1625 and 1725°C and the range of gas velocity rates permitted by substitution of up to 30% of the air with oxygen while maintaining stoichiometric fuel/oxygen ratio. Coarser, 250 to 100 micron, feed stock which in theory should yield a lower density product, was known to require somewhat higher temperatures for bubble formation so operating temperatures in the 1725 - 1825°C range, probably obtainable only with supplemental oxygen, would be maintained while feeding it. Merit of various conditions would primarily be determined by the yield of material having a true density less than one gram per cc. Lesser variables for investigation were feed rate, temperature gradient in the hot zone and means used for quenching. Only minor operating and equipment changes were made from those used in the previous campaign. These included: (1) Removal of the dome with its three inch diameter orifice from the discharge end of the furnace so that the hot combustion gases and product would be unimpeded in their discharge from the full 9" diameter of the hot zone. The turbulence caused in the gas flow by this restricting orifice had initiated and caused much more rapid slag accumulation. It was recognized that this would cause an additional radiant heat loss of ten to 15000 BTU per hour, but the previous campaign had indicated that 1800°C would still be obtainable.

(2) A conical bottom and receiver was placed on the spray chamber to permit periodic removal of product knocked down in it. (3) A larger feed-inspirating-air supply at higher pressure and a dehumidifier for this air were installed. (4) Simplified examination technique and microscopic equipment at the furnace permitted immediate evaluation of the current product and changes in operation based on these observations. (5) Provision was made for frequent flue gas analyses by operators to maintain the desired combustion conditions.

Typical operating conditions and materials distribution for this campaign are shown in Tables 3 and 4.

The float product has a true density by gas displacement of 0.77 g/cc, with insignificant variation among the three portions. It was predominantly closed bubbles less than 60μ in diameter with larger pieces, some as large as 250μ, having a frothy, multiple-bubble structure. A substantial portion of the true bubbles had smaller blisters in their skins, giving them a warty appearance.

The product having a true density greater than one g/cc was a mixture. It consisted of flaky sharp-edged feed stock which had not begun to melt, similar particles with rounded edges containing a few tiny bubbles, which together amounted to about 40% of the total; solid glass balls, most less than 20μ in diameter, amounted to 15%; bubble fragments 20%; and frothy pieces 25%.

The slag showed a range of properties from the readily friable, partially consolidated bubbles which adhered to the upper walls of the furnace to dense hard glass containing only a few bubbles which formed in parts of the furnace above 1725°C.

The furnace had to be shut down for cleaning out slag after 4000 to 8000 g had been fed. Slag formation was more rapid at the higher temperatures, but elevated temperature caused the formation of denser slag so temperature of operation had slight effect on operating time between clean-outs. The closer sizing of the feed stock used in this campaign decreased the rate of slag formation by about 30% when operating at temperatures in the range of those used in the previous campaign.

The furnace was operated 118 hours, with a total feeding time of 51 hours. The five shut-downs for clean out required 16 hours, the remainder of the time was required for heating to operating temperatures.

Fourteen thousand five hundred standard cubic feet of propane and 2300 scf oxygen were used in the campaign.

TABLE 3

Typical Operating Conditions

C_3H_8 cfm	Air cfm	O_2 cfm	Flue gas, % CO_2	O_2	CO	Furnace Temp. °C Bottom	Top	Feed Size, μ	g/min	Cyclone Product %	Volume % Float
1.2	30	0	11.6	1.6	0	1375	1100	-- (a)	--	--	--
2.0	47	0	13.2	0.2	0	1670	1370	-74+30	6	22	46 (b)
2.3	52	0	13.5	0.0	0	1730	1410	-100+30	7	26	62 (c)
2.2	50	0	13.0	0.4	0	1740	1440	-100+30	9	5 (d)	50
2.7 (f)	60	1.0	13.6	0.3	0	1740	1430	-74+30	14	18 (e)	47
2.8 (f)	58	1.2	14.2	0.0	0.3 (h)	1760	1560	-74+30	14	18 (g)	54
2.8 (f)	60	1.2	14.3	0.1	0.0	1785	1530	-74+30	13	13 (i)	40
2.7	57	1.6	14.9	0.1	0.1	1730	1500	-100+30	18	20 (j)	43
2.9	54	3.0	15.8	0.2	0.0	1800	1490	-240+100	23	8 (k)	45

(a)   Warm up conditions used to 1500°C.

(b)   Float material (density < 1.0 g/cc) all smaller than 50μ. Most of the sink material is 40 to 70μ sharp edged pieces with none to a few tiny bubbles in them, indicating start of bubble formation in these pieces. Estimated 10 volume percent of this sink material is less than 15μ diameter solid glass spheres which have been overheated.

(c)   Float material contains some larger (70μ) bubbles, and appears to have larger average bubble size than (b) above, made at 60° lower temperature. Ten to 15 volume percent is rounded frothy multiple bubble particles of 50 to 200μ diameter. Of the sink material 25 volume percent is tiny solid glass spheres less than 25μ in diameter. The balance is rounded sharp edged pieces, 40 to 100μ, containing from one to several tiny bubbles, but these bubbles are larger and more numerous than in (b) above.

(d)   Typical decrease in yield with burner port about half occluded by slag and lower third of furnace diameter reduced to 7 to 8 inches. This situation requires shutdown to remove slag.

(e)   Cooling water had to be used in spray chamber to reduce temperature of offgas to safe limit of recovery system. This decreased the yield in the cyclones, but product was later recovered from the spray chamber.

(f)   Increase in gas consumption and use of supplemental oxygen to maintain 1730-1750°C temperature was probably caused by the very high relative humidity, 85-92% RH at 90°F, of the blast air used and consequent increase in heat content of the hot gas.

(g)-(e) applied also. The float material contained 10 to 20 volume percent of +70μ bubbles and frothy pieces. The sink material contained very few pieces with sharp edges, indicating that even the largest pieces were beginning to get hot enough to melt.

(h)   Fuel-oxygen ratio had been altered to give slightly reducing conditions in order to increase the length of the hot zone without raising the temperature. This was effective, as indicated by the 200°C spread between bottom and top as compared with the 310° spread of the previous entry. This extension of the hot zone appeared effective in melting the larger pieces as noted in (g).

(i)   Float and sink fractions had same general appearance as (g). Formation of molten slag rapid under these conditions. In 70 minutes it ran down and occluded burner port.

(j)   Float and sink fractions similar to (g), with the exception that ten volume percent of the sink fraction was broken bubble fragments, thin walled, and apparently largely from +100μ bubble. This stuff looked like egg shells.

(k)   The considerable accumulation of molten slag in the furnace caught most of the product, greatly decreasing the yield. About 40% of the float fraction was > 50μ bubbles and frothy agglomerates, some 10% was > 200μ; showing that at 1800°C bubble formation from these larger particles of feed was possible. The sink material was over 60% broken fragments, most of them appeared to be from bubbles larger than 100μ. About 20% solid glass balls, some as large as 30μ, indicated that a sizeable portion of the feed had been over-heated so that once-formed bubbles had collapsed. The proportion of material overheated was probably much higher than this, since most of the molten slag which accumulated so rapidly at this temperature was formed by this mechanism.

TABLE 4

Materials Balance

Feed:	grams	%
−100 +30 μ	36500	
−240 + 100 μ	2100	
	38600	

Recovered Product:

Float, < 1.0 g/cc

	grams	%
Cyclone Product −60 + 100 m	1059	
Cyclone Product −100 m	606	
Spray Chamber Product	870	
	2535	

Sink, > 1.0 g/cc

	grams
	3360
Cyclone Product	1655
	5015

Slag:

	grams
2 August 0445	1963
3 August 0515	2850
3 August 1800	3330
4 August 1145	4283
5 August 0230	2539
5 August 1530	13195
	28160

Yield:

	%
Total Product	20.0
Product, Density <1.0 g/cc	6.5

	%
Slag:	73.0
Accounted For:	93.0

The product obtained having a density less than 1.0 g/cc had a true density of 0.77 g/cc, only 0.03 less than that of the preceding campaign. Yield of this material was 6.5% based on weight of feed. This is a modest improvement over the 4.5% of the previous campaign, but we had hoped for a much greater improvement resulting from narrower particle size distribution of the feed stock in this campaign and higher operating temperatures.

While formation of 30 to 60μ bubbles from the -74μ +30μ feed occurred at 1640 to 1700°C, it was apparent that feed particles larger than 50μ required higher temperatures for bubble formation. In the 1740 to 1800°C range, larger feed particles formed larger bubbles and frothy agglomerates, but deposition of slag was so rapid that yield decreased to the vanishing point.

Extension of the length of the hot zone in the furnace by use of neutral to slightly reducing conditions appeared to give only slight improvement in yield. Hot spot temperatures above 1775°C could not be obtained with neutral or reducing conditions.

The 25 to 30% increase in fuel requirement under high humidity conditions had not been foreseen. Dehumidification of combustion air would have been desirable.

The production of 10 to 20% fractured bubbles was not anticipated. Some of this was no doubt due to the necessary water quenching, but lower velocity gas streams would also have been desirable.

This campaign provided a fair coverage of feasible and reasonable operating conditions for the production of microbubbles from pure silica. An operating temperature of 1800°C -- 90° above the melting point of silica -- was obtained. At this temperature little unmelted material remained, but slag build up in the furnace was so rapid that only short periods of operation could be obtained. At somewhat lower temperatures -- 1640 to 1740°C, bubble formation from the finer particle sizes of feed stock was fair and rate of slag formation less. Sojourn time of the particles in the hot zone was usually about 0.25 seconds and never more than 0.4 seconds, so that much material went through without forming good bubbles. Rate of feed input had little effect on the quality of product. A fairly constant proportion of the feed ended up as slag.

The three campaigns on the direct furnace process for producing silica microbubbles have demonstrated feasibility but yields are poor and cost of product would be very high. It is anticipated that proportion of slag produced could be substantially reduced in larger units having relatively less contact of the product stream with slag coated furnace walls. We do not believe much increase in sojourn time or operating temperature is feasible without a considerable increase in the proportion of pure oxygen used.

C. Bonding of Microbubbles into Structural Shapes

The low dielectric constant and dissipation factor which are characteristic of silica are decreased in this bubble product because of the high proportion of voids filled with inert gas. It was desirable therefore to keep the density of the bonded shape as low as possible consistent with usable structural strength. Forming pressures had to be relatively low to minimize breakage of the bubble. While the bubbles survive 1000 psi hydraulic or pneumatic pressure with very little breakage, breakage was much greater in molding the semi-dry mixtures we worked with. Use of large quantities of liquid in the mix to attain uniform hydrostatic loading on the bubbles was impractical because severe shrinkage and cracks occurred when the liquid was driven out during curing. Bubble breakage as a function of molding pressure on a typical semi-plastic molding mixture was determined. Mixing followed by pressing at 100 psi caused 15% breakage, 500 psi caused 45% breakage and 2000 psi about 80% breakage. This data is shown in Figure 1.

Because of the elevated service temperature required of this material, none of the organic bonding agents were suitable and ceramic techniques had to be resorted to. The typical ceramic bond, glass, was first explored. It quickly became apparent that the bubbles were soluble in all the molten glasses tried. Because of the tremendous specific surface of the bubbles and their relatively thin walls even a small amount of solution caused collapse.

Among those tried were low melting lead glasses and some non-lead compositions such as are used for enamelling aluminum. Various combinations of oxide fluxes, particularly B_2O_3, P_2O_5 and As_2O_5, were tried, but again whenever temperatures sufficient to soften and mature the bond were attained, shrinkage and collapse of the bubbles occurred because of their solution by the molten glass.

Alkali silicate cements, which were found to give good room-temperature-setting bonds, gave structures with low dielectric constants at room temperature but specific conductivity and loss tangent increased very rapidly at temperatures above 200°C. Similar results were obtained with other cold setting cements such as magnesium oxyphosphate or chloride and calcium silicate or aluminate. This was to be expected, because all of these supply substantial quantities of mobile cations at elevated temperature which function as charge carriers.

Aluminum phosphate bonding gave rapid curing and superior green strength, but provided no bond when fired to 1150°C. It seemed possible that a silica-phosphate bond might have been formed under these conditions but this apparently did not occur. The green strength provided by the polymeric phosphate was lost when it reverted to crystalline aluminum pyrophosphate and dialuminum phosphate between 250 and 300°C.
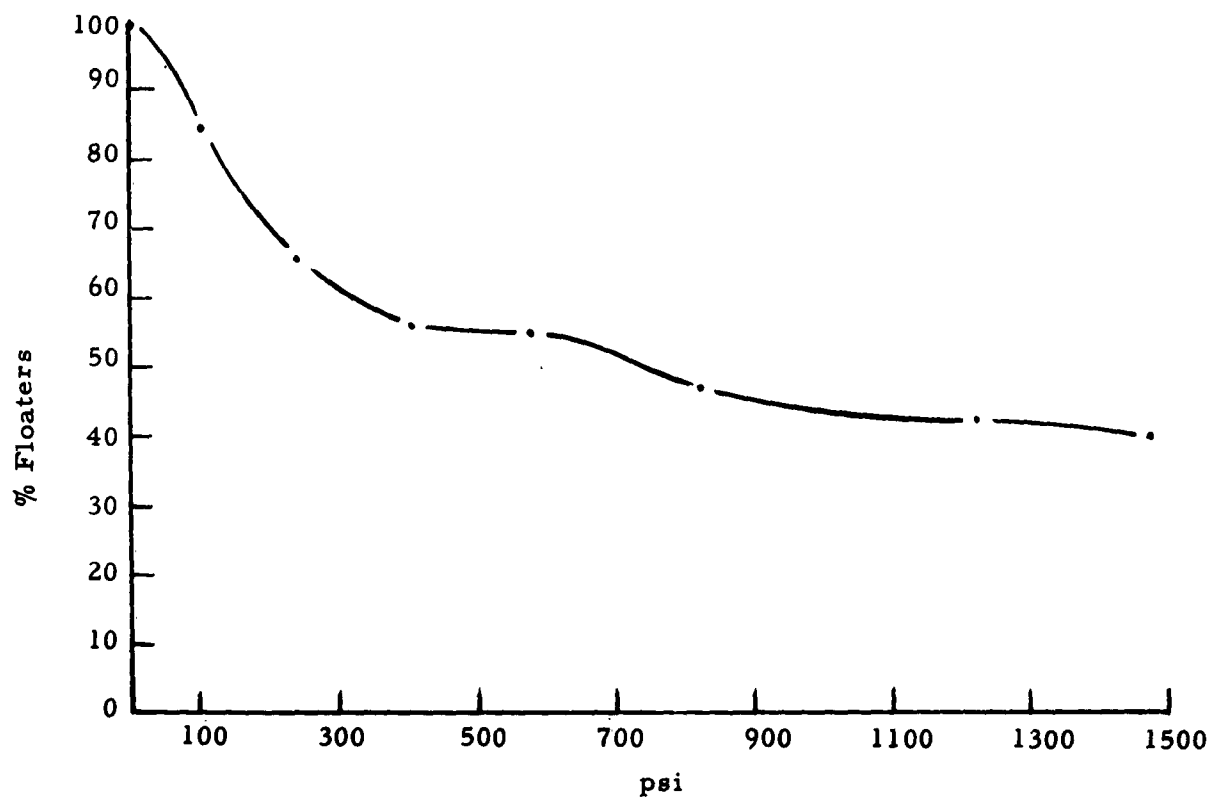
FIGURE 1

MOLDING PRESSURE vs BREAKAGE
of ECCOSPHERES SI

Bonding with a low, 0.3% sodium, silica sol gave sound low density blocks. Early work was with a 30% SiO_2 sol in amounts up to 150% of the weight of silica bubbles. Low pressure, 50 to 150 psi, at room temperature was used for molding. The green bond was very weak and the ten to 20% drying shrinkage caused break-up of most pieces in this operation. Addition of gelling agents such as volatile or decomposable acids or acidic salts and alkaline earth silicates gave some improvement in bond strength, but drying shrinkage still caused much loss.

It was then found that extremely thorough mixing while using care to avoid segregation of the alkaline earth gelling agent was necessary. Also, use of much smaller quantities of the silica sol greatly decreased the shrinkage, while bond strength was maintained.

Further decrease in water content as molded was obtained by the use of 50% silica sol obtained from Nalco Chemical Company as Nalcoag 1050. Adequate dispersal of the relatively small volume of silica sol, only 4 to 10 volume percent of the batch, could not be obtained in the light fluffy mass by ordinary mixing techniques without excessive breakage of the bubbles; but it was found that repeatedly forcing the damp mix through a four-mesh screen gave a uniform mixture without much breakage.

A very slow drying schedule, starting with an 80-90% humidity atmosphere at 30 to 40°C and gradually decreasing the humidity during 6 to 10 days to a dry atmosphere, almost eliminated the drying cracks.

The dried blocks were strong enough to fire to 1070°C on a fairly rapid schedule.

The alkali silicate gelling agent used certainly was not improving the dielectric properties of the product so a purified ball clay was substituted for it. This gave a slight improvement in green and cured strength. These blocks were partially vitrified in firing to 1070°C.

It was eventually found that both gelling agent and clay could be eliminated by use of somewhat higher molding pressures and addition of a very small amount, about 0.03% of the batch weight, of polyvinyl alcohol (Elvanol 51-05 duPont) as a dilute aqueous solution.

Attempts were made to use a proprietary alumina-silica sol said to contain about 20% alumina (Nalcoag LR-111 of the Nalco Chemical Company) in the hope that finely dispersed alumina would react with the silica of the bubbles and form a mullite-type bond. No bonding was obtained in firing to 1100°C.

Similar unsatisfactory results were obtained with a zirconia sol, (Zirconia Sol 180 from duPont) but an ammonium zirconyl carbonate solution containing

TABLE 5

Preparation and Physical Properties of Bonded Microbubble Blocks

Ref. No.	Size (a)	Bond Mtl. (b)	Bond %(c)	Additives (d) Mtl. %	Mtl. %	Mold P. psi	Firing Hrs.	Firing °C.	Lin. Shr. %	Dens. g/cc	Break S. psi	Remarks	Firing Test 18 hrs. to 1400°C.; 2 hrs. at 1400°C. Break S. psi	Lin. Shr. %
19	m	SS	20	Act 10		166	8	1100	4.	.38	205	Some small drying cracks	14 (Total) Locally fused spots due to poor dispersion of activator.	
20	m	SS	75	Act 10	BC 10	166	8	1100	3.5	.55	685	No cracks		
21	s	SS	55	Act 10	Ben10	408	1	1200	4.0	.65	1140	One small drying crack		
23	s	SS	60	Act 10	Ben10	408	3	1100	3.5	.82	875	No cracks		
25	s	SS	60	Act 10	Ben10	490	3	1100	3.0	.79	1130	No cracks		
26	s	AS	60	BC 10		600	1	1100	3.0	.86	1545	One firing crack cf. 20		
27	s	AS	45	BC 10		815	1	1100	7.0	.65	400	Fine hairline cracks		
28	s	AS	50			900	2	1100				Poor green strength		
29	s	AS	45			730	2	1100				No bond on firing		
39	m	SS	25	Act 10		408	1.5	1160	4.0	.55	215	No cracks		
39	m	SS	25	Act 10		165	1.5	1160	5.0	.41	106	No cracks		
41	m	SS	25	Act 10	BC 10	165	3	1130	14.	.48	480	Severe shrinkage during firing		
49	m	SS	25	Act 10		165	3	1130	4.5			Hairline cracks from drying		
52	l	SS	75		BC 10	175	2.5	1130	4.5			Many small drying cracks		
57	l	SS	35	Act 10		200	3	1260				Severe warpage and cracking in firing		
58	l	SS	35	Act 10		220	4	1160	3.5	.43		Hairline cracks from drying		
65	m	SS	50	Act 10		230	2	1160	5			Many hairline cracks		
67	m	Zr	23			230	2	1160	7	.50	1100	Severe firing shrinkage and cracks but vitreous bond		
73	s	SS	50	BC 10		1225	4	1100	4	.95	1950	No cracks cf. 20		
73	l	SS	50	BC 10		500	2	1100	4.5	.67	1100	No cracks cf. 20		
74	l	SS	50	BC 10		300	2	1100	4.0	.60	975	A few surficial drying cracks		
75a	m	SS	50	BC 10		166	2	1100	4.5	.38	660	One edge crack	33 Warped. Dispersion of clay poor	
75b	m	SS	50	BC 10		232	2	1100	4.5	.48	770	No cracks		
75d	m	SS	50	BC 10		365	2	1100	4.5	.62	710	No cracks		
75e	s	SS	50	BC 10		327	2	1100	3.5	.41	878	No cracks		
79	s-m	AP	50			500	4	1250	3.5	.54	340	No cracks	11 Some pock marks	
79	s-m	AP	50			200	4	1150	5.	.33	56	No cracks		
85	m	Zr	25			1960	3	900	3.5	1.02	4670	Few drying cracks		
85	m	Zr	25			500	3	900	4.5	.55	1255	Some drying cracks		
86	s-m	Zr	15			1960	3	900	4	1.04	3420	One drying crack	4 No enlargement of cracks. Barely vitrified	
86	s-m	Zr	15			500	3	900	5	.56	540	Many drying cracks		
90	s	SS	50			1000	2	1150	3	.73	2460	No cracks	2 A few small cracks. Uniform	1410
90	m	SS	50			500	2	1150	4.5	.69	1040	One drying crack		
91	m	SS	75			300	1	1150	4.5	.58	1520	No cracks		
94	s-m	Zr	25			700	1	950	4.	.53	1060	Two firing cracks		
94	s-m	Zr	23			500	1	950	4.5	.72	2820	No firing cracks		
92	m	Zr	10	PWA 0.1		300	1	950	4.5	.46	635	Three firing cracks	Cracks enlarged. A few new ones.	217

The following is a data table rotated 90° on the page. Column headings are not printed; the table is transcribed by position.

Block	Bond	Size	%	Additive							Remarks		Remarks
95	Zr	s	20		700	1	950	3.5	.65	1845	This group had poor green strength and developed drying cracks	2210	No new cracks. No shrinkage
95	Zr	m	20		500	1	950	5.	.55	1460			
96	Zr	m	20		1960	3	950	3.5	.94	3630			
96	Zr	m	20		800	3	950	5.	.64	1570			
98	Zr	m	20		1380	2	1100	4.	.68	2280			
98	Zr	m	20		800	2	1100	4.	.70	2410			
100	SS	m	75		1200	2	1170	3	1.01	3275	No cracks		
100	SS	m	75		250	2	1170	3.5	.52	960	No cracks	3610	0.5 Two new cracks
101	Zr	m	15	PVA 0.6	1060	1	925	5.5	.80	4600	No cracks		
101	Zr	m	15	PVA 0.6	330	1	925	4.5	.46	1500	One small crack	557	1.5
105	SS	m	50	PVA 0.5	1060	1	1100	4.	.70	1280	No cracks		
108	SS	m	30		1060	1	1100	3.	.80	1600	No cracks		
109	SS	m	30	PVA 0.1	1060	1	1050	3.	.81	1200	Two small cracks		
110	SS	m	20	PVA 0.1	1960	2	1100	2.	1.06	4280	Three large firing cracks		
110	SS	m	20	PVA 0.1	1060	2	1100	3.	.92	2140	Five small firing cracks		
110	SS	m	20	PVA 0.1	330	2	1100	4.	.52	725	Numerous small firing cracks		
111	SS	s	45	PVA 0.1	1960	4	1150	1.5	1.05	2500	No cracks (e)	2320	<0.5 Three small cracks
112	SS	s	50	PVA 0.1	1385	4	1150	2.5	1.07		No cracks	2960	1.0 Some vitrefication
112	SS	s	50	PVA 0.1	1960	4	1150	1.5	.94	2030	Three cracks	890	No shrinkage, no cracks
112	SS	sm	50	PVA 0.1	1062	4	1150	3.0	.79		Multiple hairline cracks	320	<0.5 New hairline cracks
113	SS	m	33	PVA 0.1	332	4	1150	3.0	.51		Two large cracks		
114	SS	s	45	PVA 0.1	1635	4	1150	0.0	.84		No cracks	820	<1.0 Vitrefied
115	Zr	s	15	PVA 0.1	1960	4	1150	0.0	.84	318.	Broke in two pieces while-firing	380	<1.0 One new crack
117	SS	s	50	PVA 0.1	1960	2	1400	0.2	1.02		No cracks, no pinholes		
118	Zr	s	75	PVA 0.1	1960	2	1400	0.2	.84		Few tiny edge cracks		
119	SS	s	65	PVA 0.1	1960	2	1400	1.5	1.20		No cracks, no pinholes		Partially vitrefied

(a) Sizes: s = 9 sq. in., m = 20 sq. in., l = 50 sq. in.

(b) Bond Materials: SS = Silica Sol 30% SiO2 Ludox 19-26, 50% SiO2 Natcoag 1050 subsequently
AS = Alumina sol Natcoag LR-111; Zr = Ammonium Zirconyl carbonate sol'n. 10% ZrO2
AP = Mono aluminum phosphate sol'n. 30%

(c) All percentages based on Microbubble weight only.

(d) Additives: Act. = Alkaline earth silicate. Pennsylvania Salt Co. Activator 05,
BC = Ball clay, Ben. = Bentonite, PVA = polyvinyl alcohol,
Elvanol 51-05 duPont

(e) Blocks 112-119 incl. made from direct process microbubble.

10% ZrO_2 (Titanium Alloys & Metal Divi$. on of National Lead Corp.) caused severe shrinkage and vitrification at 1180°C. Decreasing the ZrO_2 addition to 1.5% of the mix rather than the 15% used origin' lly and cutting the firing temperature to 900°C brought the firing shrinkage down to about 4%, but still gave a nice vitreous bond. The surprising thing about this bond was that no more shrinkage or softening orccurred when it was refired at 1400°C. We have no real explanation for the difference in behavior of the two zirconia preparations. It may be that much better distribution of the zirconia on the silica bubbles was obtained with the second preparation since it was a true solution when dispersed on the bubbles.

Composition, fabrication, and physical properties of typical cold-set-cement bonded structures are given in Table 5. Usually each composition was molded at three pressures since the density-strength relation was one of the most important in this investigation. Molds having about 9, 20 or 50 square inches cross section normal to the pressing direction were used. As in most ceramic work, the various stresses incurred in forming, drying and firing are greatly increased as the size of the piece is increased. Consequently, the appearance of cracks in pieces of differing size at the successive stages of the process provided useful information.

The 50% silica sol as binder without the addition of gelling agent, and the 10% ZrO_2 ammonium zirconyl carbonate solution proved to be the best bonds. Slow drying of the fragile green structure was essential. It was necessary to start the cure at a relati\e humidity near 80%. When this was done, the initial drying temperatures of 35 to 42°C could be used. Frequently incipient drying cracks too small to be detected before firing would open up during firing. Both bonding agents gave usable fired strengths over a considerable range of densities.

There is a definite relation between density and breaking strength as indicated in Figure 2. The spread in these data is considerable, indicative of incipient flaws in the blocks.

Hot Molding of Microbubbles: The cold set cement bonding technique used always gave a product with a high percentage of open pores. This porosity, ranging from 25 to 55 volume percent is undesirable in the anticipated electronic application because it permits moisture absorption from humid atmospheres and change of dielectric properties.

Hot molding of microbubbles was undertaken to obtain a low porosity product. In this technique, preheated bubbles are compressed in a heated mold at a temperature such that the bubbles are soft and deform without breaking. This forms surfaces of contact between the bubbles rather than the tangential contacts obtained with the cementing technique and results in much lower porosity.
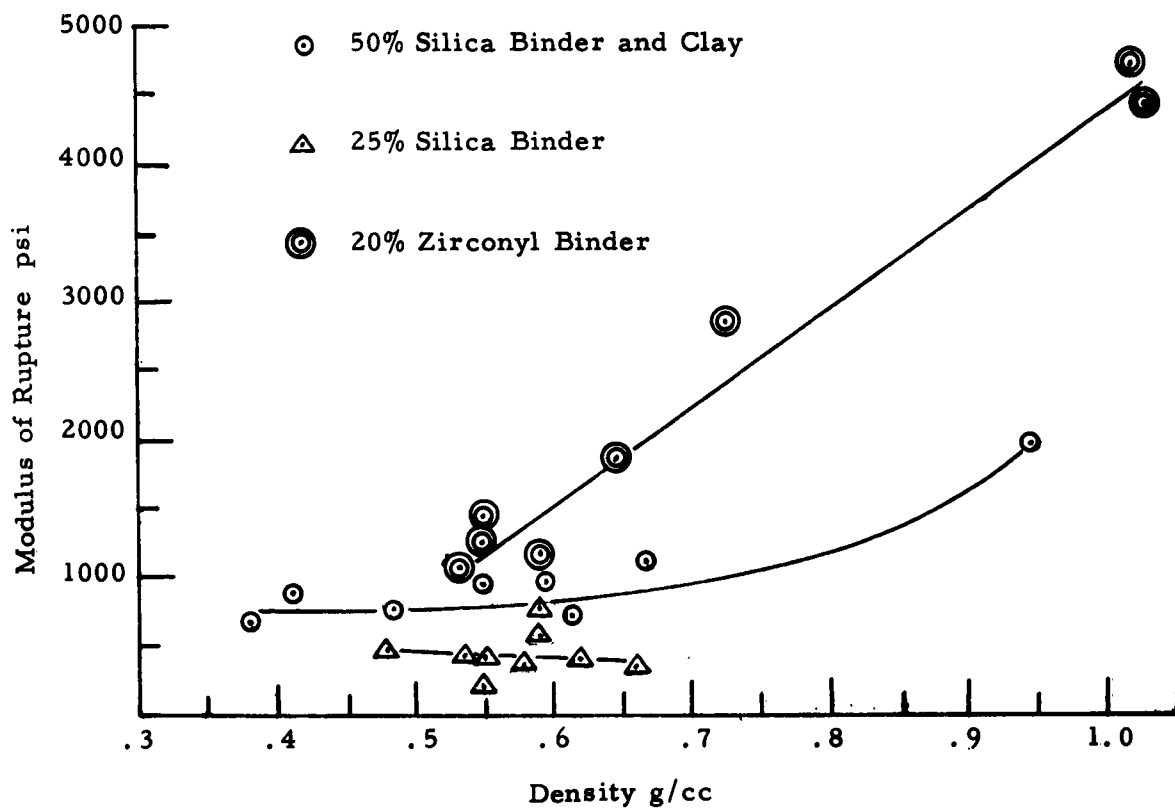
FIGURE 2

DENSITY vs BREAKING STRENGTH
of BONDED ECCOSPHERES SI

Most of this work was done with regular 16% Na Eccospheres rather than the acid leached product.

The loose bubbles were preheated to 400°C, poured into a type 303 steel mold at 700°C and after holding from two to six minutes in the mold compressed using 1100 psi pressure. The piece was ejected and annealed at 400°C. Porosities of two to three volume percent at densities of 1.2 to 1.3 g/cc were ordinarily obtained. In a few cases porosities as low as 0.25% were obtained in the same density range. Breaking strength of the molded pieces was 2000 to 4000 psi. A lower molding temperature, 550°C, and a pressure of 1100 psi gave pieces having a density of 0.7 to 0.8 g/cc and porosities of 25 to 35 volume percent.

Numerous attempts to bond the higher melting low sodium content bubbles gave very poor to non-existent bonding. Attempts to operate the mold at temperatures much above 700°C caused seizure and sticking of the plunger in the mold. Coating the working surfaces with molybdenum disulfide or a suspension of boron nitride in water glass permitted somewhat higher operating temperatures, but mold deformation was serious and no well bonded pieces were obtained. Use of a graphite mold at a higher temperature (probably 1100 to 1300°C would be required) in an inert atmosphere would certainly have made possible the bonding of this higher melting product. Equipment was not available to do this.

An attempt was made to increase the melting point of the low porosity hot molded pieces by prolonged leached in acid. Pieces of hot molded 16% sodium Eccospheres of less than 2, 5 and 12 volume percent porosity were leached with agitation of the acid for a week in cold 16% HCl, washed free of acid and dried. When fired for two hours at 700°C about 20% shrinkage occurred in the 12% porosity piece but it retained its shape. The less porous pieces collapsed, with the formation of a considerable amount of solid yellowish glass in the center of the least porous piece. It was apparent that the less porous material did not permit adequate penetration of the acid to remove much of the interior sodium.

D. Electrical Properties of Microbubbles

Dielectric Properties of Bulk Microbubbles: Material prepared by acid leaching 16% sodium "Eccospheres" by several procedures as well as pure silica microbubbles made in the direct high temperature process were determined at several frequencies and temperatures up to 500°C.

An outline of the procedures used on the materials follows:

a. Eccospheres SI (ESSI): Water floated 16% Na Eccospheres were transferred wet to 16% H_2SO_4. Two grams 98% H_2SO_4 per gram of dry Eccospheres

was used. Water that was added with the wet Eccospheres diluted the acid to about 12%. The slurry was stirred for four hours to keep the floating Eccospheres mobile and wet by the solution. The acid was drained off and the Eccospheres washed with water until the washings were neutral to indicator paper. The product was centrifuged and dried at 90 to 125°C.

b.   Eccospheres H_2SO_4, (ES, H_2SO_4): Regular 16% Na Eccospheres were leached with intermittent agitation for 120 days in 98% H_2SO_4 using 10 g of acid per g of Eccospheres. The product was washed free of acid and dried 72 hours at 150°C.

c.   Eccospheres HCl, (ES, HCl): Regular 16% Na Eccospheres were leached 120 days in 37% HCl using 6 g of acid solution per g of Eccospheres. The product was washed free of acid and dried 72 hours at 150°C.

d.   Eccospheres HCl (b) (ESHCl b): Eccospheres SI were leached for 6 days with continuous agitation in 16% HCl at 100 to 105°C using 8 g of acid solution per g of Eccospheres. The product was washed free of acid and dried 72 hours at 150°C.

e.   Eccospheres SI dehydrated (ESSI dehy.): Eccospheres SI were heated in a 1 cm deep layer for 16 hours at 900°C and 8 additional hours at 1140°C.

f.   Eccospheres HCl (b) dehydrated (ESSI dehy.): Dehydrated by heating on the same schedule as the previous sample.

g.   Silica Microbubbles by direct process (DP)

All samples measured at 8.6 kmc were placed in the 19 mm. deep powder cups used to terminate the wave guide and compacted lightly by vibrating the cup. Packed densities of the samples as measured consequently vary somewhat. The weight and volume of the sample as measured were determined. Assuming the true density of all samples to be 2.2 g/cc (that of vitreous silica) volume percent solids of each sample as measured was determined.

TABLE 6

Dielectric Properties of Bulk Microbubble Products

Temperature, °C	Vol. % solids	25°		100°		200°		300°		400°		500°	
Material		K	Tan d	K	Tan d	K	Tan d	K	Tan d	K	Tan d	K	Tan d
ESSI	5.3	1.18	0.0050	1.19	0.0064	1.19	0.0062	1.17	0.0035	1.16	0.0028	1.16	0.0039
ES H$_2$SO$_4$	4.8	1.17	0.0069	--	--	--	--	--	--	--	--	--	--
ES HCl	4.7	1.16	0.0079	--	--	--	--	--	--	--	--	--	--
ES HCl (b)	4.5	1.14	0.0056	1.15	0.0078	1.15	0.0064	1.14	0.0041	1.13	0.0025	1.13	0.0022
ESSI dehy.	4.6	1.11	0.00025	1.12	0.00073	1.11	0.00021	1.11	0.00060	1.11	0.00095	1.11	0.0017
ES HCl b dehy.	4.5	1.13	0.00045	1.13	0.00029	1.13	0.00051	1.13	0.00015	1.13	0.00070	1.13	0.0013
Microbubble DP	9.5	1.21	0.00057	1.22	0.00071	1.22	0.00097	1.22	0.00085	1.22	0.00085	1.22	0.00067

Although extractable alkali was undetectable in the more vigorously leached materials such as ES HCl (b) loss tangents remained similar to ESSI containing 0.9% extractable Na and 3.7% total Na.

The fact that the loss tangents did not decrease in spite of removal of all extractable sodium was disappointing. It was speculated that in leaching sodium might be replaced with hydrogen, leaving a slightly hydrated silicic acid and that this was responsible for the persistently high loss tangents. It is known that some forms of silica do not completely lose combined water at temperatures even of 100.0°C. The direct process microbubble, while made from a silica sol the same way the other products were, had been exposed to a much higher temperature and could presumably be more completely dehydrated. It was decided to heat the leached products to as high a temperature as was available in an effort to dehydrate it and improve the dielectric properties thereby. The results of this heating and dehydration are shown on the dehydrated (dehy.) samples. At all temperatures except 500°C these have equivalent or lower losses than those of the DP product, indicating that this dehydration results in a product dielectrically equivalent to the direct process microbubble. These loss tangent values are an order of magnitude smaller than those on the best leached material before high temperature dehydration.

While all microbubble samples were dried at 150°C and cooled in a dry atmosphere before running dielectric tests, it was found necessary to maintain an essentially dry atmosphere in the measuring chamber at low frequencies. The much more pronounced effect of absorbed moisture on dielectric properties at low frequencies, the high specific surface of these materials and their somewhat hygroscopic tendency made results highly erratic unless this measure was observed.

TABLE 7

Dielectric Properties of Bulk Microbubble Products at Low Frequencies
in dry Nitrogen, 25°C

Frequency, cy/sec:		10^2		10^5	
Material	Solids Vol. %	K	Tan d	K	Tan d
Eccospheres SI	5.1	1.27	0.008	1.25	0.002
Eccospheres HCl	4.4	1.21	0.009	1.21	0.002
Microbubble DP	9.3	1.23	0.003	1.22	0.001

Dielectric constants of these materials are similar at the packing densities measured, but the direct process material would have a desirably lower dielectric constant than the other materials if it could be produced in their density range. The loss tangent data continues to show less loss even at these low frequencies, for the direct process product than for the leached material.

E. Electrical Properties of Microbubbles in Structural Shapes

Specific resistivity, and its change with temperature was used as a screening procedure for various bonding schemes. Elevated temperature properties of these materials were of primary concern. Since dielectric losses generally have a temperature trend similar to conductivity and conductivity is much easier to measure over an extended temperature range, it was used for screening of bond types.

Trends of specific resistivity of the various bonding types with temperature are shown in Figures 3 and 4.

This plot of log of specific resistivity versus the reciprocal of the absolute temperature shows similar slopes for all the bond types particularly at the higher temperatures. This indicates ionic conduction by the same or at least similar mechanisms in all cases regardless of the bond type. In contrast, a vitreous silica foam formed directly from molten silica (Pittsburgh Corning's Foamsil) has a very flat temperature resistivity curve indicating almost complete absence of mobile charge carriers at the highest temperature tested. This is what we sought but did not find with our bonded materials.

Dielectric properties of several of the better bonded structures are shown in Tables 8 and 9.
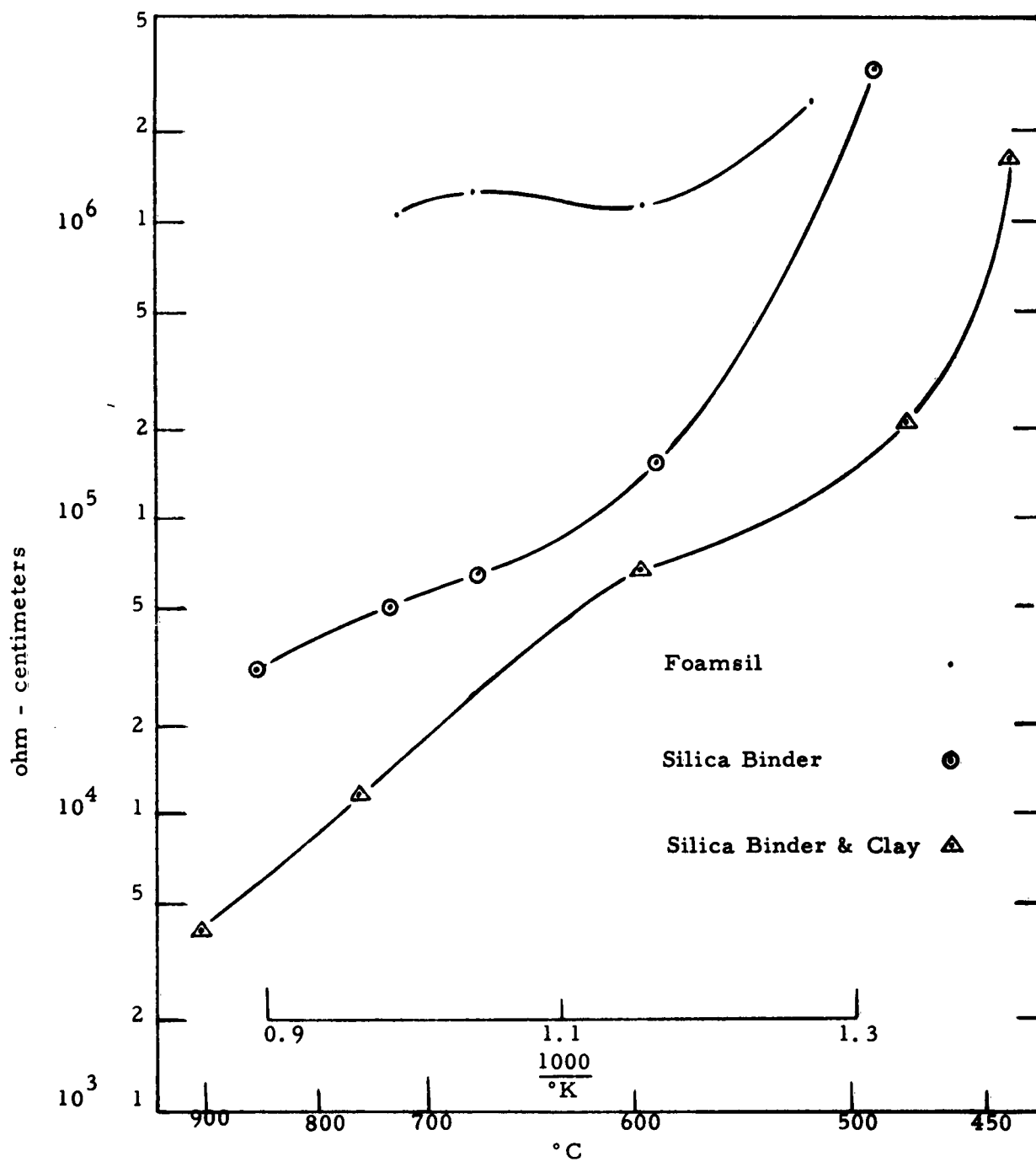
FIGURE 3

SPECIFIC RESISTIVITY AS AFFECTED BY TEMPERATURE OF
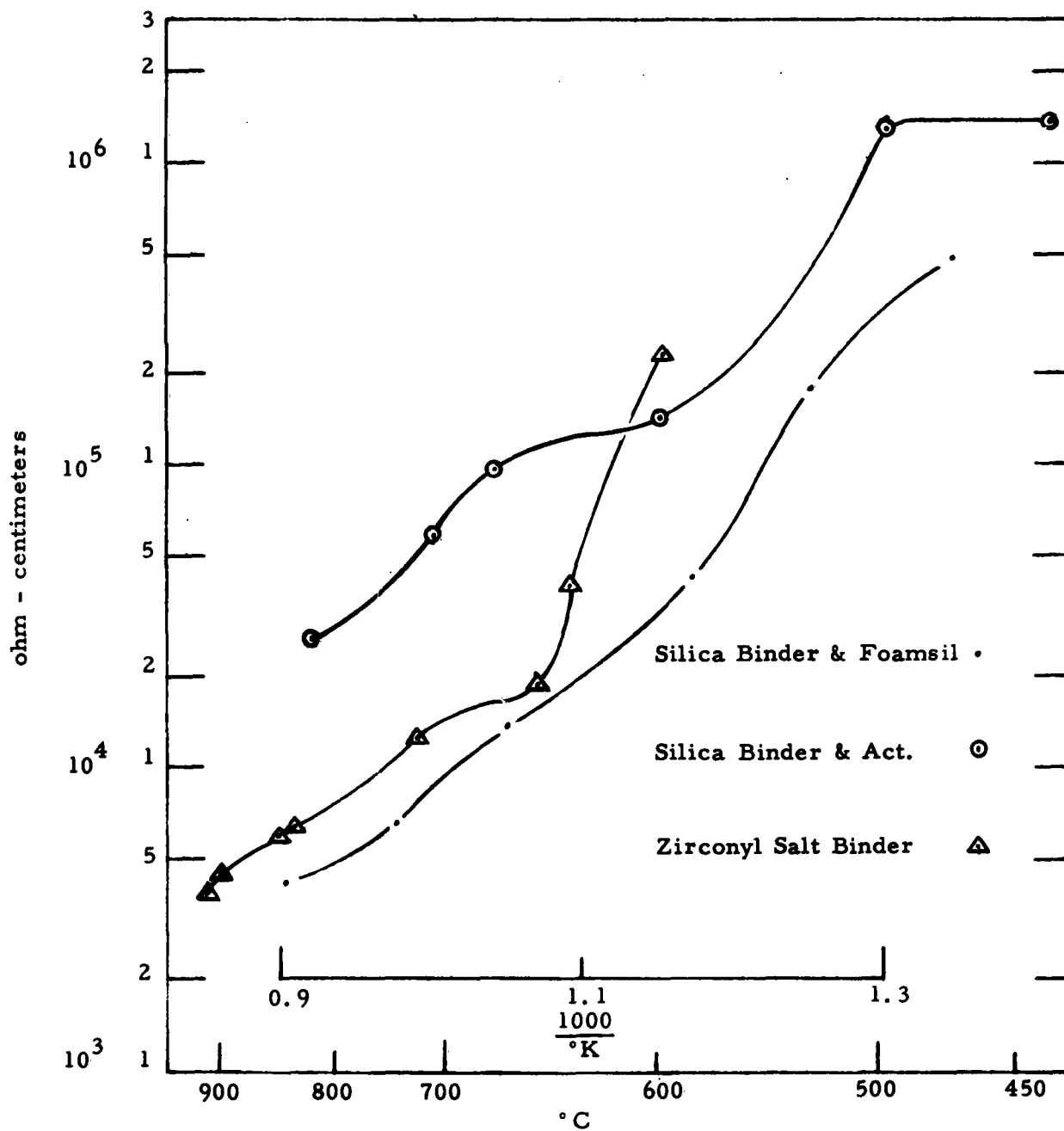ECCOSPHERE SI STRUCTURES MADE WITH VARIOUS BONDS

FIGURE 4

SPECIFIC RESISTIVITY AS AFFECTED BY TEMPERATURE OF
ECCOSPHERE SI STRUCTURES MADE WITH VARIOUS BONDS

TABLE 8

Dielectric Properties of Bonded Eccospheres SI at 8.6 kmc and Various Temperatures

Temperature, °C	25°		100°		200°	
Material No. (a)	K	Tan d	K	Tan d	K	Tan d
19	1.40	0.0030	1.41	0.0036	1.41	0.0070
20	1.59	0.0034	1.59	0.0024	1.60	0.0024
112-1150	2.05	0.0029	2.08	0.0033	2.10	0.0045
112-1400	1.99	0.0022	2.00	0.0015	2.02	0.0016

Temperature, °C	300°		400°		500°	
Material No. (a)	K	Tan d	K	Tan d	K	Tan d
19	1.42	0.016	1.44	0.012	1.42	0.032
20	1.60	0.015	1.62	0.027	1.64	0.025
112-1150	2.10	0.0060	2.12	0.0088	2.11	0.021
112-1400	2.02	0.0041	2.04	0.011	2.03	0.016

(a) Numbers refer to materials in Table 5. 19 contains about 6% total alkali. 20 contains about 4% total alkali and 10% ball clay. 112 contains less than 4% total alkali. Both samples were fired 4 hours at 1150°C. 112-1400 was fired an additional two hours at 1400.

As was foreshadowed by the specific resistivity data, no particular improvement was obtained with the lower alkali content alone, but some decrease in dielectric loss was obtained by firing to 1400°C.

TABLE 9

Dielectric Properties of Bonded Eccospheres SI at Low Frequencies and 25°C in Dry Atmosphere (a)

Frequency, cy/sec:	10^2		10^5	
Material	K	Tan d	K	Tan d
65 (b)	1.72	0.0134	1.68	0.0016
75 (c)	1.79	0.017	1.71	0.0054

(a) These data obtained by the Laboratory for Insulation Research, Massachusetts Institute of Technology, by Mr. W. B. Westphal. The samples were dried at 200°C, cooled and measured in a dry nitrogen atmosphere.

(b) and (c) Numbers refer to materials in Table 5. (b) contains about 6% total alkali and is comparable to No. 19 of Table 5. (c) contains about 4% total alkali and 10% ball clay. It is comparable to No. 20 of Table 5.

The higher dielectric constants and loss tangents at these frequencies as compared with those at 8 kmc is fairly typical of many high silica glasses.

III CONCLUSIONS

Silica microbubble material has been produced by two routes. The direct 1700°C process yields dielectrically excellent material: dielectric constant 1.22 ± 0.01 over the frequency range 10^2 to 10^{10} cycles per second and loss tangents decreasing from 0.003 at 10^2 to 0.0006 at 10^{10}. At 10^{10} cy/sec dielectric constant remains constant and loss tangent remains less than 0.001 up to 500°C. This material has a true density by gas displacement of 0.8 g/cc. Acid leaching of sodium borosilicate glass bubble made at 950°C followed by dehydration at 1140°C gave a product having a slightly lower dielectric constant, and loss tangent equivalent to the direct process material except at temperatures above 400°C where the loss tangent become 0.002. It had a true density of 0.26 g/cc. Yields were very poor by the direct process, primarily because of losses as slag. The acid leaching method is much less expensive. Since it yields a product substantially equivalent dielectrically at one-third the density, this is the preferred route.

Both products withstand moderate loads continuously at 1100°C and do not collapse at 1300°C.

These products can be bonded into simple low density structural shapes without serious degradation of dielectric properties.

A material unique in its very low dielectric constant and loss that retains its utility at over 1000°C has been produced in bulk form and bonded structures. The process is simple and readily expanded to quantity production.

EMERSON & CUMING, INC., Canton
Massachusetts
THE DEVELOPMENT OF SILICA HOLLOW
MICROSPHERES FOR USE AS A HIGH
TEMPERATURE DIELECTRIC, by J. W.
Lefforge and R. S. Lothrop. 27 p. incl. figs.
and tables (Project 7371: Task 73710)
(WADD TR 60-899 Part II) Contract AF33
(616)-7263   July 1961   Unclassified Report

Silica microbubble material has been pro-
duced by two routes. The direct process
melts particles of silica and expands them
into bubbles at 1700°C. Yields of only 5%,
primarily because of loss as slag, excessive
fuel requirements, and the relatively high

(over)

true density, 0.8 g/cc, of the product, made
the other process the more desirable one.
Acid-leaching of 16% sodium glass bubbles
which are made commercially at 950°C,
followed by dehydration at 1140°C gave a
product having a true density of 0.26 g/cc.
It had a slightly lower dielectric constant,
1.11 to 1.2, and equivalent loss tangent
values, less than 0.001, at all frequencies
and temperatures below 400°C. Both
materials were bonded into sheet structures
using cold set cement type bonds without
serious degradation of the dielectric proper-
ties. These structures withstand moderate
loads at 1100°C and do not collapse at 1300°
C. Densities range from 0.6 to 1.2 g/cc.